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## Pressure-induced chemistry for the 2D to 3D transformation of zeolites

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**ADOR, an unconventional synthesis strategy based on a four-step mechanism: assembly, disassembly, organization, and reassembly, has opened new possibilities in zeolite chemistry. The ADOR approach led to discovery of IPC family of materials with tuneable porosity. Here we present the first pressure-induced ADOR transformation of the 2D zeolite precursor IPC-1P into fully crystalline 3D zeolite IPC-2 (OKO topology) using a Walker-type multianvil apparatus under pressure of 1 GPa at 200 °C. Surprisingly, the high-pressure material is of lower density (higher porosity) than the product from simply calcining the IPC-1P precursor at high temperature, which produces IPC-4 (PCR topology). The sample was characterized by PXRD, <sup>29</sup>Si MAS NMR, SEM, and HRTEM. Theoretical calculations suggest that high pressure can lead to the preparation of other ADOR zeolites that have not yet been prepared.**

Zeolites are microporous aluminosilicates with pores and cavities of molecular dimensions.<sup>1</sup> More than 230 unique zeolite structures had been recognized by the International Zeolite Association;<sup>2</sup> however, there are millions of possible, theoretically predicted frameworks,<sup>3</sup> which makes the synthesis of new zeolites a continuing challenge. Zeolites are predominantly synthesised using hydrothermal approaches,<sup>4</sup> but alternative preparative techniques have been developed, such as ionothermal synthesis<sup>5</sup> and the ADOR method.<sup>6</sup> The development of the ADOR process (Figure 1) has opened new possibilities in zeolite chemistry.<sup>7,8</sup> This strategy includes four steps: 1) A – assembly of the 3D zeolite structure, 2) D – disassembly of the parent zeolite into layered precursor by hydrolysis, 3) O – organization of layers into a more ordered arrangement, 4) R – reassembly of the 3D into a structure that is different to the parent zeolite. The ADOR strategy is more complicated than solvothermal methods and requires multi-step synthesis, however it is more controllable and some of the zeolites can be produced exclusively by this method.<sup>7</sup>

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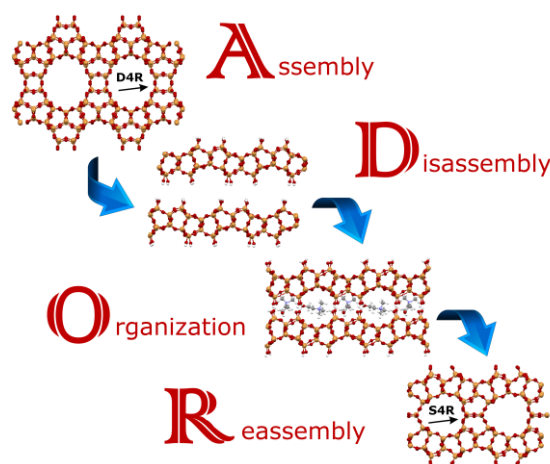
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**Figure 1.** Schematic representation of ADOR process. 'A' stands for assembly of the parent UTL (with D4R units) structure, 'D' – disassembly to IPC-1P zeolite precursor, 'O' – organizing by intercalation of organics, and 'R' – reassembly by calcination (in this example to IPC-2 (OKO), with S4R units).

The ADOR strategy exploits the instability of germanosilicate parent zeolites allowing the disassembly of the structure. The germanosilicate with the **UTL** topology<sup>9, 10</sup> has silica layers connected by double four ring (D4R) units that contain almost all the Ge-centred tetrahedra. Hydrolysis in acidic media allows removal of the D4Rs with preservation of silica layers producing the layered zeolite precursor IPC-1P.<sup>8</sup> Reassembly of the IPC-1P layers can produce a family of zeolites with controlled porosities; ranging from small pore IPC-4 (**PCR** topology) to the larger pore IPC-2 (**OKO** topology).<sup>6</sup> Through controlled organisation of the layered precursors<sup>11</sup> one can also prepare other materials: IPC-6,<sup>12</sup> IPC-7,<sup>13</sup> IPC-9, and IPC-10.<sup>14</sup> The ADOR process can also be applied to other parent zeolites, such as germanosilicate **UOV**.<sup>15, 16</sup>

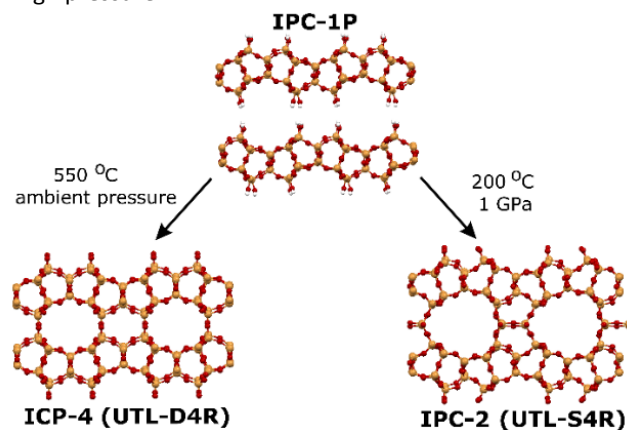
The intermediate layered precursor IPC-1P can be isolated from Ge-**UTL** after the disassembly step. The key to preparing the different 3D materials from IPC-1P is control over the organisation and reassembly steps. The simplest method of connecting the IPC-1P layers into a 3D zeolite is to calcine the system at above 500 °C (Figure 2). The high temperature condenses the silanol groups on the surface of the IPC-1P layers, producing Si-O-Si linkages that connect the layers into the 3D zeolite and releasing water.<sup>6</sup> The topology of the material formed is IPC-4 (**PCR**), the expected product from simple condensation of IPC-1P layers. The relationship between this material and the original **UTL** parent is that IPC-4 has lost the entire D4R unit from between the layers. We therefore can also describe the **PCR** topology as **UTL-D4R**.

Another new way of zeolite synthesis was presented by Jordá *et. al.* as a phase transition process.<sup>17</sup> The high-pressure conditions were applied on ITQ-29 zeolite inducing the transformation to novel ITQ-50 zeolite. It was the first pressure-induced 3D → 3D zeolite transition. The previous high-pressure experiments on zeolites led to the amorphization of the material, not producing the ordered phase.<sup>18</sup>

Here we present the first application of high-pressure conditions beyond those of hydrothermal chemistry to induce the 2D → 3D transformation of zeolites. IPC-1P layers were treated in a Walker-type multianvil apparatus<sup>19, 20</sup> at 1 GPa with heating at 200 °C applied for 2 min. After the treatment the sample was allowed to cool and the pressure slowly released. The product was characterized using PXRD, <sup>29</sup>Si MAS NMR, SEM, and HRTEM. Surprisingly, the obtained material was not IPC-4 but PXRD (Figure 3) identified the product as IPC-2 (with the **OKO** topology); a less dense member of IPC family of zeolites. Compared to the initial **UTL** parent IPC-2 can be described by the overall loss of only a single four ring (**UTL-S4R**). This is particularly interesting as to form IPC-2 requires that extra silicon must end up between the layers to form the S4R linkers (Figure 2).

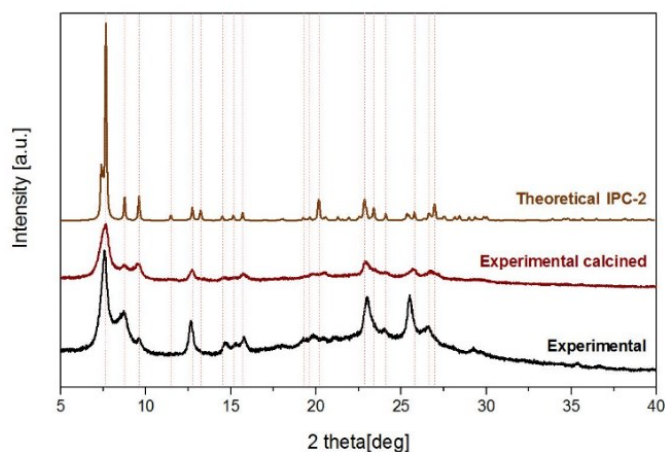
In previous work on the ADOR process, IPC-2 can be realized in two ways: 1) the rearrangement of the structure of **UTL** germanosilicate in hydrochloric acid,<sup>21</sup> or 2) the alkoxysilylation of IPC-1P, using diethydimethoxysilane in 1M nitric acid at hydrothermal conditions.<sup>6</sup> However, using the high-pressure synthesis we describe here does not require use of any solvent and the transformation is induced by high-pressure at the

relatively low temperature of 200 °C. The material recovered after the high-pressure synthesis can also be calcined at high temperature. The PXRD of the calcined sample shows no change in the position of the diffraction peaks, although there are some changes in relative intensities (Figure 3). The uneven baseline of the experimental PXRD pattern could indicate the presence of traces of amorphous silica in the material obtained by the use of high pressure.

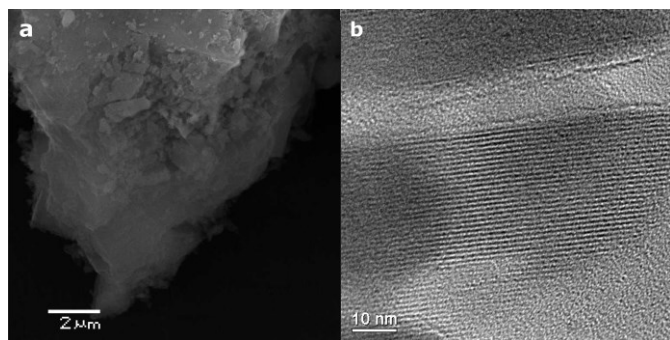


**Figure 2.** Transformation of IPC-1P layered precursor under high-temperature and high-pressure conditions into IPC-4 (density = 1.87 g/cm<sup>3</sup>) using calcination and into IPC-2 (density = 1.75 g/cm<sup>3</sup>) using high pressure.

SEM images (Figure 4a) show the morphology of the crystals after recovery from the high-pressure cell. IPC-2 zeolite obtained by standard ADOR synthesis has plate-like crystals with the shape similar to the original, parent **UTL** zeolite.<sup>10</sup> The crystals of the sample obtained by the pressure-induced method have different shape (see ESI Figure S2.); they are less well defined. Most probably this is because of the extreme conditions of the treatment, which resulted in loss of the plate-like shape after the application of the high pressure. The TEM image (Figure 4b) shows the connected 1 nm thick layers with the d-spacing of 1.2 nm, which corresponds to the IPC-2 (**OKO**) zeolite model.

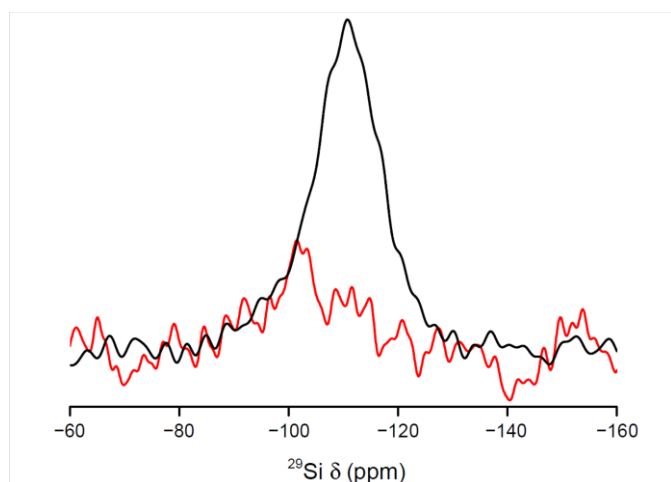


**Figure 3.** X-ray diffraction powder patterns of IPC-2 zeolite synthesized under high-pressure conditions (black), after further calcination (red), and theoretical one (brown). The positions of the main peaks of the theoretical pattern are indicated by the vertical lines.



**Figure 4.** SEM (a) and HRTEM (b) images of IPC-2 zeolite synthesized under high-pressure conditions. The measured d-spacing (1.2 nm) corresponds to the theoretical model of **OKO** zeolite.

Calcined, high-pressure synthesized IPC-2 was also examined by  $^{29}\text{Si}$  MAS NMR (Figure 5). The analysis of the spectrum showed two types of species:  $\text{Q}^4$  ( $\text{Si}(\text{OSi})_4$ ) and  $\text{Q}^3$  ( $\text{Si}(\text{OSi})_3(\text{OH})$ ) species visible at  $\delta = -111$  and  $-102$  ppm, respectively. A cross-polarization (CP NMR) spectrum confirms the presence of  $\text{Q}^3$  species (Figure 5). Most of the silicon is in  $\text{Q}^4$  form ( $\approx 90\%$ ), however in the ideal scenario, fully connected 3D IPC-2 (neglecting the effect of external surface), has no  $\text{Q}^3$  sites (*i.e.* the  $\text{Q}^4/\text{Q}^3$  ratio is infinite). This means that the IPC-2 synthesized at high pressure has remaining silanols ( $\approx 10\%$ ) that are not fully condensed in the final calcined solid. The IPC-2 made using the high-pressure method described here is therefore more defective than the more ideal samples prepared using other methods.



**Figure 5.**  $^{29}\text{Si}$  (14.1 T, 30 kHz MAS) NMR spectrum of calcined IPC-2 zeolite synthesized under high pressure (black, 1280 scans) and the  $^{29}\text{Si}$  (14.1 T, 30 kHz MAS) CP NMR spectrum of it (red, 8192 scans).

The key to control the phase transition was application of the accurate conditions that induced the condensation of layers without their decomposition. The formation of IPC-2 was obtained under the specific pressure, time, and temperature. To have a better understanding of the behavior of IPC-1P under various conditions the series of experiments were performed. The results are collected in the Table 1.

**Table 1.** The influence of the pressure, temperature, and time of the treatment of IPC-1P layered zeolite precursor on the final product.

Pressure [GPa]	Temperature [°C]	Time [min]	Resulting phase
1	RT	-	IPC-1P
1	700	20	Quartz
1	550	20	Quartz
1	550	2	Quartz
5	500	2	Coesite
1	400	2	Amorphous
1	300	2	Amorphous
1	250	2	Amorphous/IPC-2
1	200	2	<b>IPC-2</b>

The trial at room temperature under 1 GPa pressure did not cause any structure transformation and the resulting phase was unchanged IPC-1P. Pressures of 1 GPa at 550–700 °C resulted in the complete recrystallization of the IPC-1P to quartz. The transformation is completed in 2 min. This transformation indicates that at high temperatures and pressures of  $\sim 1$  GPa, the bonds in IPC-1P are labile enough to break quickly and allow the rearrangement needed for the formation of quartz.<sup>22</sup> An increase in pressure up to 5 GPa at 500 °C drove the system towards the well-known high pressure phase coesite production.<sup>23</sup> Using the same pressure (1 GPa) but a lower temperature of 250 °C caused the amorphization of the sample. The direct formation of IPC-2 from IPC-1P is a surprising result. IPC-4 has a higher density than IPC-2 (1.87 g/cm<sup>3</sup> and 1.75 g/cm<sup>3</sup> respectively). Theoretically, in the absence of other considerations, high-pressure experiments should favor more dense phases, and given that there is an available pathway for the formation of IPC-4 one might imagine that this would be the product. The thermal calcination of IPC-1P without any intercalated organics, under ambient pressure, led to formation of pure, well crystalline IPC-4. In addition, at first glance the IPC-1P material does not have enough silicon to form the S4Rs that are required to link the layers together in the final material. So the questions raised by the formation of IPC-2 are: why does the system not produce the denser IPC-4 and where does the extra silicon come from to form the S4R units that link the layers together in the final structure? Of course, the first thing to note is that high pressure minimizes the volume of the whole system and not just the solid. The condensation of the silanols into silicate linkages produces water, and this must also be accommodated in the system as a whole. This is likely the reason why IPC-2 is favored under these pressure conditions: the volume of the whole system (zeolite plus water) is lower when the zeolite is IPC-2 because more water can be accommodated in the pores than can be accommodated in the smaller pores of IPC-4.

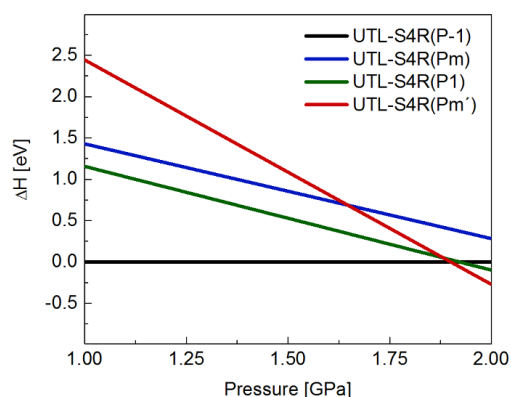
Taking the question of where the silicon comes from to make the extra S4R units, the  $^{29}\text{Si}$  MAS NMR results shows the defective nature of the sample, however it is not possible to define the position of defects. It should be noticed from Table 1 that the combination of pressure plus temperatures above 250 °C is clearly enough to break the Si–O bonds in the materials and



instigate rearrangement process. This is the only way to explain the formation of amorphous materials and the dense phase silicas such as quartz and coesite. Therefore, it would be of no real surprise to see that temperatures almost as hot (200 °C) and the same pressures (1 GPa) may also induce some rearrangement of the system. Indeed, this must be the case as there is no extra silicon in the system that could account for the final product – the silicon in the S4R units must come from the IPC-1P itself. This idea is further confirmed by the change in morphology seen in the SEM. There seems to be substantial changes to the crystals themselves, and so a rearrangement process is very likely. This is in marked contrast to the usual ADOR process, where such large-scale rearrangement has not been seen. There is always the possibility of the presence of small amounts of amorphous silica in the original IPC-1P starting material, and the crystallization of this material into IPC-2 may also drive the minimization of the volume. However, there is little evidence for extensive amorphous impurity in the sample of IPC-1P.

There are other possible rearrangement products that show similar overall structures of **UTL**-type layers linked via S4R units and the targeting of such previously unknown materials is one of the great advantages of the ADOR approach.<sup>24</sup> For the **UTL**-derived layers found in IPC-1P there are four possible ways of connecting the layers into new zeolites; two of these have been realized experimentally but two have not.<sup>6,14</sup> Therefore, the thermodynamic stability of the four possible products of condensation via S4R bridges at high pressure was investigated computationally (see ESI for further details). Calculations carried out at the density functional theory (DFT) level show that the IPC-2 (**OKO**) zeolite is the most stable up to 1.8 GPa (Figure 6), in agreement with experimental findings.

A further goal would be the pressure-induced synthesis of the other possible ADOR products. Calculations show that zeolites with new topologies could be obtained at pressures above 1.8 GPa (Figure 6). This is perhaps the most intriguing aspect of the current study, and further work is ongoing in this area to identify the correct conditions. Of particular interest is the material that is of lowest energy at higher pressure (listed as **UTL-S4R(Pm')** in Figure 6 is currently unknown experimentally.



**Figure 6.** Enthalpy vs. pressure curve for **UTL-S4R** zeolites (IPC-1P layers connected with S4R units). Relative energies  $\Delta H$  are with respect to IPC-2 (**OKO**). Notation adopted from Ref.<sup>6</sup>

Yet another possibility is to find experimental conditions that lead to synthesis of zeolites obtained by direct condensation of IPC-1P layers, such as IPC-4 (**PCR**). The crucial point to control the transformation may be the organization step of the ADOR-type high-pressure synthesis. It can be studied by the intercalation methods, further optimization of the synthesis conditions, or use of different zeolitic precursors.

## Conclusions

The results presented here show the first pressure-induced synthesis of a regular 3D zeolite from 2D precursor. It is also an extension of the ADOR zeolite synthesis procedure. In contrast to calcination under ambient pressure, the high-pressure conditions unexpectedly produced a more porous phase, IPC-2, rather than the expected denser IPC-4. This new use of high pressure in the ADOR process opens a new route that can lead to the synthesis of many predicted zeolite structures that cannot be accessed by standard methods. Those new structures are interesting due to high framework energies and very rare, odd-member ring channels that can be exploited in catalysis and sorption. The high-pressure ADOR approach is precise and controllable method allows to reach the synthesis targets beyond the scope of the solvothermal synthesis.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgement

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